

High pressure – high temperature studies and reactivity of γ -Mo₂N and δ -MoN

D. Machon¹, D. Daisenberger¹, E. Soignard², G. Shen³, T. Kawashima⁴,
E. Takayama-Muromachi⁴, and P. F. McMillan^{*,1,5}

¹ Department of Chemistry and Materials Chemistry Centre, University College London, 20 Gordon Street, London, UK

² Department of Geological Sciences, Arizona State University, Tempe, AZ 85287-1404, USA

³ GSECARS, Advanced Photon Source, Argonne National Laboratories, Argonne, Illinois, USA

⁴ National Institute for Materials Science, Superconducting Materials Center, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

⁵ Davy-Faraday Research Laboratory, The Royal Institution of Great Britain, 21 Albermarle Street, London, UK

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A combination of high pressure – high temperature synthesis and laser-heated diamond anvil cell experiments, using synchrotron X-ray diffraction has been used to investigate the phases in the Mo₂N–MoN system under these conditions. Under conditions of high nitrogen activity, δ -MoN appears to be a limiting phase i.e. there is no evidence for formation of new compounds such as Mo₃N₄ or Mo₃N₅, that are encountered in the Zr–N, Hf–N or Ta–N systems. When γ -Mo₂N is heated or prepared under conditions of high N₂ activity, δ -MoN is formed. The results indicate (a) that there is no stable cubic stoichiometric “ γ -MoN” phase formed even under conditions of high pressure – high temperature and high N₂ activity, and (b) that no solid solution is formed between γ -Mo₂N and δ -MoN.

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1 Introduction

Transition metal nitrides are refractory materials that possess technologically useful properties including superconductivity and high hardness. The stable and metastable phase relations and the high temperature – high pressure stability of many of these important compounds still remain to be established, however. This is especially true within the Mo–N system [1, 2]. To date, known MoN_x phases include the stoichiometric hexagonal compound δ -MoN, a non-stoichiometric cubic phase γ -Mo_{2-x}N, and perhaps a high temperature distorted cubic β -MoN_y phase with $y \sim 0.25$ – 0.3 (Fig. 1) [1, 2].

δ -MoN is a high-hardness material with very low compressibility (its bulk modulus, K_0 , was recently measured to be 345 GPa) [3]. It is also a superconductor with T_c attaining 12–15 K, depending upon the preparation conditions and the degree of structural order [4, 5]. Synthesis routes often result in a hexagonal compound with space group P6₃mc, with nitrogen atoms disordered among the anion sites formed by the metal sublattice (Fig. 2). This material has a superconducting $T_c \sim 4$ K [4, 5]. Annealing at high pressure and high temperature, or direct synthesis under high pressure – high temperature conditions, results in ordering of the nitrogen atom positions to give hexagonal δ -MoN with the same space group symme-

* Corresponding author: e-mail: p.f.mcmillan@ucl.ac.uk

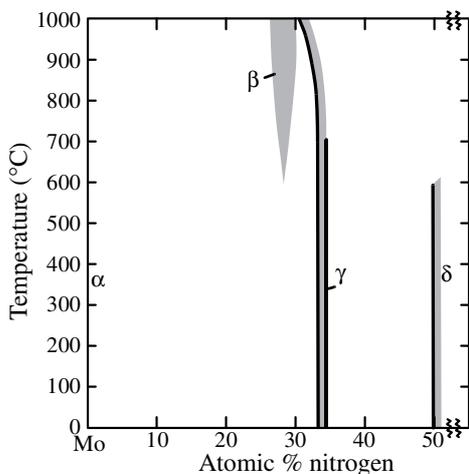


Fig. 1 Phase diagram of the Mo–N system at $P = 1$ atm, redrawn from Toth [1]. The existence of the “ β -MoN_x” phase, that is proposed to have a cubic or tetragonally distorted structure, is not yet well established [1].

try ($P6_3mc$), but with a doubled c -axis parameter [4, 5]. The ordered structure has a much higher superconducting transition temperature ($T_c = 12–15$ K [4, 5]).

The cubic γ -Mo₂N phase has a B1 structure based on that of NaCl, with $\sim 50\%$ of the anion sites vacant (Fig. 2). Materials prepared under conditions of low nitrogen activity [6] can exhibit greater degrees of nitrogen deficiency, and the vacant sites can be ordered, resulting in lower symmetry materials including tetragonal or orthorhombic distortions from the cubic cell [1]. γ -Mo₂N is found to be superconducting with $T_c \sim 5$ K. The related cubic nitride NbN possesses a very high T_c value (17 K) [7], that constituted a record among binary compounds prior to the recent measurements on MgB₂ [8]. It has been predicted that if a fully-stoichiometric cubic compound γ -MoN could be obtained, it would have T_c values that might attain 29.4 K [9]. However, a stoichiometric cubic γ -MoN phase has not yet been demonstrated in any synthesis experiments carried out to date. Theoretical calculations by Hart and Klein [10] have indicated that a fully-stoichiometric γ -MoN phase with the B1 structure would always present elastic instabilities and never be stable. However, it is possible that distorted B1 structures, or structures with larger unit cells, might be prepared by appropriate synthesis routes.

It is known that application of high pressures, including generation of high N₂ activity during synthesis experiments, can be used to achieve formation of new dense nitrides with high nitrogen contents (e.g.,

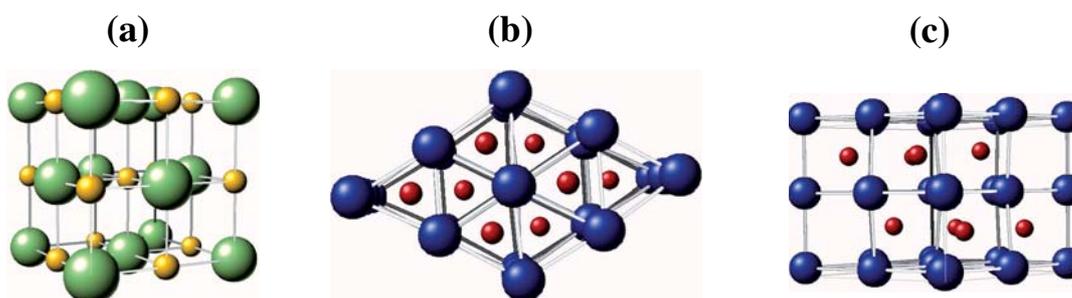


Fig. 2 (online colour at: www.pss-a.com) (a) B1 (NaCl) structure with space group $Fm\bar{3}m$ that provides a base structure for γ -Mo₂N. In the nitride, vacancies occur on the anion sites (smaller spheres). Ordering among the anion vacancies can result in lowered symmetries for γ -Mo_{2-x}N materials, such as $Pm\bar{3}m$ [1]. The compounds can also exhibit tetragonal, orthorhombic or possibly trigonal distortions from cubic symmetry. (b) The hexagonal ($P6_3mc$) structure of ordered δ -MoN, projected down the c -axis and (c) normal to c . Note the ordering of the N atom positions in consecutive layers parallel to the c -axis. In disordered δ -MoN samples, the N positions are not completely ordered, and the average c -axis dimension is halved, although the space group is unchanged.

Zr₃N₄ and Hf₃N₄ [11], PtN [12]). Zhao and Range [13] first carried out a high pressure – high temperature synthesis of MoN compounds by reacting MoO₃ and NH₄Cl at $P = 2$ GPa and $T = 1500$ °C; that synthesis yielded single phase hexagonal δ -MoN. Zhang and Leinenweber at Arizona State University [14] reacted Zn₃N₂ + MoCl₃ mixtures under similar conditions ($P = 1.0$ GPa; $T = 700$ °C); however, cubic γ -Mo₂N was obtained. The X-ray diffraction peaks were broadened, indicating formation of nanocrystalline material with an average particle size ~ 10 nm. Syntheses at higher pressures ($P = 4$ – 6 GPa) resulted in formation of hexagonal δ -MoN ([4, 5, 14]).

It was of interest to determine the relative stability of δ -MoN and γ -Mo₂N phases as a function of the pressure and the temperature, and also the possible formation of intermediate compounds *via* high pressure – high temperature experiments. Here we have used a combination of high pressure – high temperature synthesis and laser-heated diamond anvil cell (DAC) experiments, using synchrotron X-ray diffraction to investigate the phases in the Mo₂N–MoN system under these conditions.

2 Experimental procedures

Single phase Mo₂N was obtained from High Purity Chemicals, Japan. This compound exhibited an orthorhombic distortion from cubic symmetry (Fig. 3). This sample was then used to prepare well-crystallized cubic γ -Mo₂N following high pressure – high temperature treatment in a flat belt type apparatus at 7.7 GPa and 1673 K [15]. This cubic sample was used to determine the bulk modulus of well-crystallized γ -Mo₂N, and was also used as a starting material for laser-heated DAC experiments carried out at the Advanced Photon Source.

In situ X-ray diffraction experiments and high pressure – high temperature syntheses were carried out within cylindrical symmetric diamond anvil cells using double-sided laser heating techniques to achieve high temperature [16, 17]. Powdered starting materials were pressed into thin plates and loaded cryogeni-

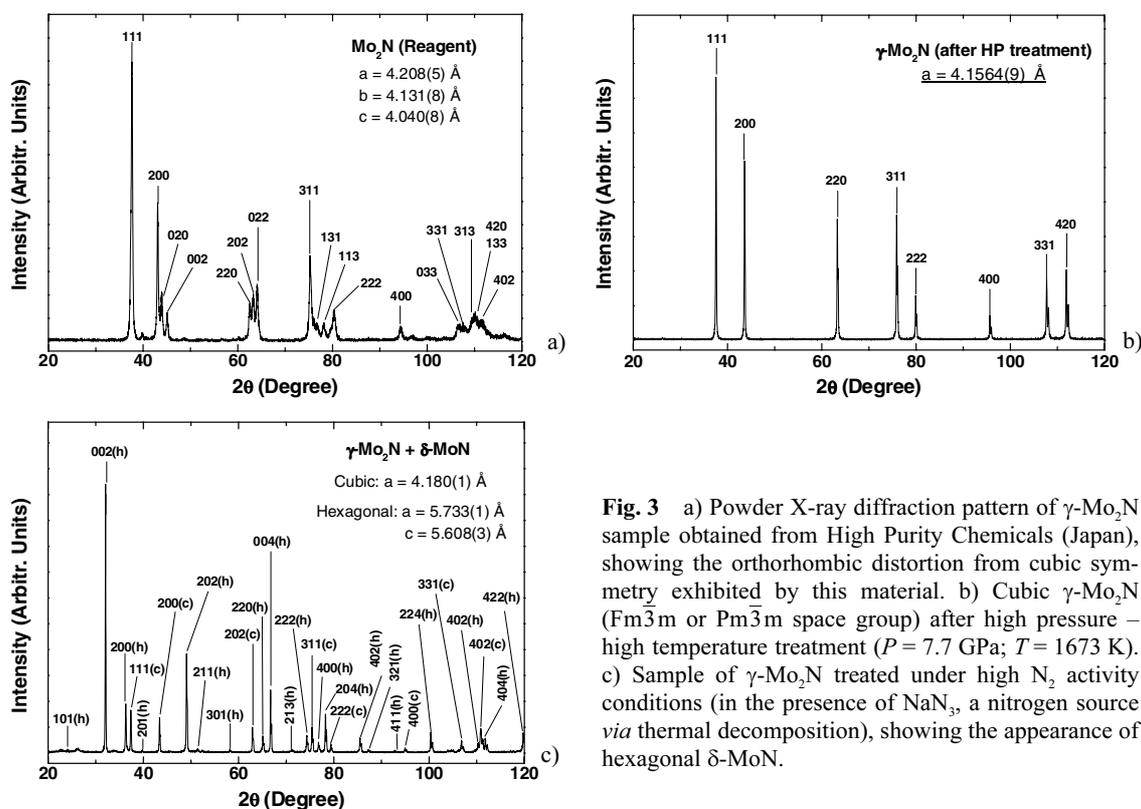


Fig. 3 a) Powder X-ray diffraction pattern of γ -Mo₂N sample obtained from High Purity Chemicals (Japan), showing the orthorhombic distortion from cubic symmetry exhibited by this material. b) Cubic γ -Mo₂N (Fm $\bar{3}$ m or Pm $\bar{3}$ m space group) after high pressure – high temperature treatment ($P = 7.7$ GPa; $T = 1673$ K). c) Sample of γ -Mo₂N treated under high N₂ activity conditions (in the presence of NaN₃, a nitrogen source *via* thermal decomposition), showing the appearance of hexagonal δ -MoN.

cally with either N₂ or Ar as pressure-transmitting media, to provide reactive vs. non-reactive sample environments.

Diamond culet faces were generally ~200 μ m in diameter and the samples were contained within a 90 μ m hole drilled in a Re gasket. Samples were pressurized to between 20–80 GPa before laser heating, during high pressure – high temperature synthesis runs. Several μ m-sized ruby crystals were also loaded into the cells for pressure determination *via* the Cr³⁺:Al₂O₃ fluorescence method [18]. *In situ* X-ray diffraction measurements were performed at the ID13–GSECARS beamline of the Advanced Photon Source (Argonne National Lab., Illinois, USA), using angle-dispersive techniques with monochromatic radiation ($\lambda = 0.3344$ Å). Diffraction patterns were collected using an image plate detector (MAR345). The sample-to-detector distance and image plate inclination angles were calibrated with a CeO₂ standard. The 2-D diffraction data were integrated around the diffraction rings and transformed to fully-averaged 1-D plots using the Fit2D software [19].

Samples were heated simultaneously from both sides with a Nd³⁺:YLF laser, using a maximum power of 80 W and spot size of 20–30 μ m at the sample surface [20]. Temperatures during the laser heating runs were obtained from grey-body fits to the thermal emission spectra measured between 400–950 nm.

3 Results and discussion

First, the compression of this well-crystallized material was used to determine a bulk modulus value for the γ -Mo₂N phase. Figure 4a shows V/V_0 as a function of pressure with argon as pressure-transmitting medium. This data are fitted using a third-order Birch–Murnaghan equation of state with $K_0 = 304(1)$ GPa with $K'_0 = 4.0(2)$. These values were obtained using a F – f plot (Fig. 4b) i.e. representing the data in terms of the Eulerian strain parameter (f) and normalized pressure (F), i.e.,

$$f = \frac{1}{2} \left[\left(\frac{V}{V_0} \right)^{-2/3} - 1 \right],$$

$$F = P[3f(1 + 2f)^{2.5}]^{-1}.$$

This formalism yields the second-order finite strain equation

$$F = K_0[1 - 1.5(4 - K'_0)f].$$

The values $K_0 = 304(1)$ GPa and $K'_0 = 4.0(2)$ were estimated from the intercept and the slope, respectively.

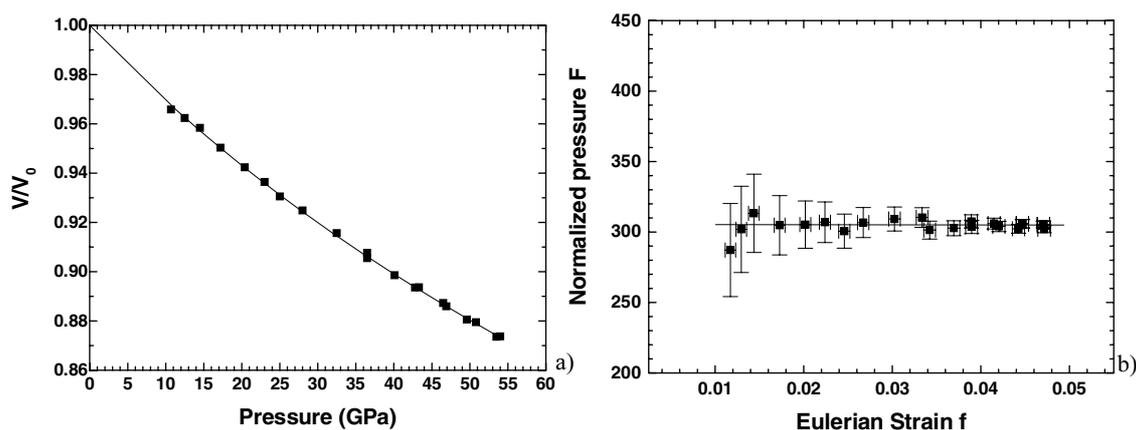


Fig. 4 a) Plot of measured V/V_0 for γ -Mo₂N as a function of pressure along with a 3rd order Birch–Murnaghan equation of state fitted to the data with $K_0 = 304(1)$ GPa and $K'_0 = 4.0(2)$. b) Plot of the normalized pressure (F) as a function of Eulerian strain (f) for γ -Mo₂N showing zero slope of the data points, consistent with the value $K'_0 = 4.0(2)$ obtained with the fitting procedure.

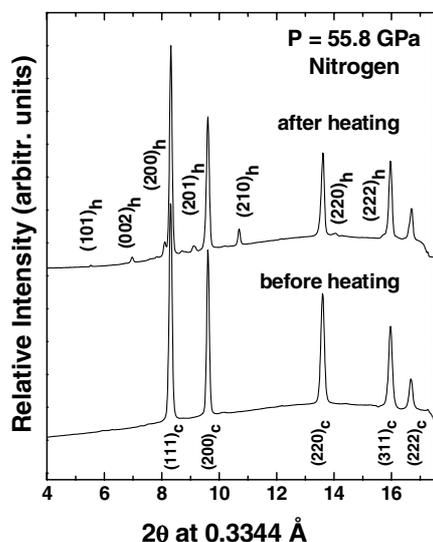


Fig. 5 Diffraction patterns of cubic γ -Mo₂N compressed in nitrogen to 55.8 GPa before and after laser-heating. The new features in the diffraction pattern are indexed to the ordered hexagonal δ -MoN structure. The refined cell parameters are $a_h = 5.40(1)$ Å and $c_h = 5.45(1)$ Å. These values are in good agreement with the ones in Ref. [3].

One sample was loaded into a DAC and pressurized to 54.1 GPa with Ar as a pressure-transmitting medium, and then laser-heated to $T = 2000$ K for 10–15 minutes. No change was observed in the diffraction patterns, indicating that this sample of γ -Mo₂N did not undergo any change under these high pressure – high temperature conditions. A similar sample was then loaded into a DAC with a N₂ pressure medium, and pressurized progressively to 55.8 GPa followed by laser-heating at $T = 2000$ K for 10–15 minutes. The X-ray diffraction patterns from the sample after heating showed extra peaks due to the appearance of hexagonal δ -MoN (Fig. 5). These results indicate that stoichiometric δ -MoN, with a hexagonal symmetry, is a limiting phase within the Mo–N symmetry at intermediate compositions. Additional high pressure – high temperature synthesis experiments were carried out within the belt press at NIMS (Japan) ($P = 7.7$ GPa; $T = 1673$ K) using commercial Mo₂N starting materials and NaN₃ as a nitrogen source. These experiments resulted in formation of coexisting γ -Mo₂N + δ -MoN phases (Fig. 3).

5 Conclusions

We investigated the high pressure – high temperature stability of γ -Mo₂N and δ -MoN by a combination of synthesis and laser-heated diamond anvil cell experiments, using N₂ or Ar as reactive vs. non-reactive pressure-transmitting media. Synchrotron X-ray diffraction was used as probe technique to observe the coexistence and stability ranges of γ -Mo₂N and δ -MoN and to detect the formation of any new phases.

Under conditions of high nitrogen activity, e.g., during laser heating DAC experiments with N₂ as a pressure medium, δ -MoN appears to be a limiting phase i.e. there is no evidence for formation of new compounds such as Mo₃N₄ or Mo₃N₅, that are encountered in the Zr–N, Hf–N or Ta–N systems [1, 11]. When γ -Mo₂N is heated or prepared under conditions of high N₂ activity (DAC experiments in a N₂ pressure medium, or synthesis experiments in the presence of a nitrogen source such as NaN₃), δ -MoN is formed. The diffraction data indicate that this is the fully-stoichiometric phase. The results indicate (a) that there is no stable cubic stoichiometric “ γ -MoN” phase formed even under conditions of high pressure – high temperature and high N₂ activity, and (b) that no solid solution is formed between γ -Mo₂N and δ -MoN. Metathesis reactions, such as MoO₃ + NH₄Cl or Zn₃N₂ + MoCl₃ can yield either δ -MoN or γ -Mo₂N, depending upon the synthesis conditions and the choice of precursors. The products can be nanocrystalline, and/or structurally disordered. High pressure – high temperature treatment results in improved crystallinity.

Bulk moduli of nanocrystalline and microcrystalline γ -Mo₂N are shown to be similar (301 GPa [3] and 304 GPa, respectively).

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References

- [1] L. E. Toth, *Transition Metal Carbides and Nitrides* (Academic Press, New York, 1971).
- [2] G. Hägg, *Z. Phys. Chem. B* **7**, 339 (1930).
- [3] E. Soignard, P. F. McMillan, T. D. Chaplin, S. Farag, C. L. Bull, M. Somayazulu, and K. Leinenweber, *Phys. Rev. B* **68**, 132101 (2003).
- [4] A. Bezinge, K. Yvon, J. Muller, W. Lengauer, and P. Ettmayer, *Solid State Commun.* **63**, 141 (1987).
- [5] C. L. Bull, P. F. McMillan, E. Soignard, and K. Leinenweber, *J. Solid State Chem.* **177**, 1488 (2004).
- [6] The chemical potential of nitrogen can be expressed by $\mu_{N_2} = \mu_{N_2}^0 + RT \log(a_{N_2})$ where $a_{N_2} = \gamma x_{N_2}$ is the nitrogen activity, γ is the activity coefficient and x_{N_2} is N₂ molar concentration.
- [7] D. A. Papaconstantopolos, W. E. Pickett, B. M. Klein, and L. L. Boyer, *Nature* **308**, 494 (1984).
- [8] J. Magamatsu, M. Nakagawa, T. Muranaka, Y. Zenitani, and J. Akimitsu, *Nature* **410**, 63 (2001).
- [9] D. A. Papaconstantopolos, W. E. Pickett, B. M. Klein, and L. L. Boyer, *Phys. Rev. B* **31**, 752 (1985).
- [10] G. L. W. Hart and B. M. Klein, *Phys. Rev. B* **61**, 3151 (2000).
- [11] A. Zerr, G. Miehe, and R. Riedel, *Nature Mater.* **2**, 185 (2003).
- [12] E. Gregoryanz, C. Sanloup, M. Somayazulu, J. Badro, G. Fiquet, H.-K. Mao, and R. J. Hemley, *Nature Mater.* **3**, 294 (2004).
- [13] X. Zhao and K.-J. Range, *J. Alloys Compd.* **296**, 72 (2000).
- [14] Z. Zhang and K. Leinenweber, unpublished data.
- [15] T. Kawashima et al., in prep.
- [16] G. Shen, H.-K. Mao, and R. J. Hemley, 3rd NIRIM International Symposium on Advanced Materials (ISAM '98), National Institute for Research in Inorganic Materials (1996), p. 149.
- [17] E. Soignard, Ph.D. thesis, University College of London (2003).
- [18] H.-K. Mao, J. Xu, and P. M. Bell, *J. Geophys. Res.* **91**, 4673 (1986).
- [19] A. P. Hammersley, S. O. Svensson, M. Hanfland, A. N. Fitch, and D. Häusermann, *High Press. Res.* **14**, 235 (1996).
- [20] G. Y. Shen, M. L. Rivers, and Y. B. Wang et al., *Rev. Sci. Instrum.* **72**, 1273 (2001).